Synthesis of 3 Mol% Yttria Stabilized Zirconia (3YSZ) and Study on Corrosion Behavior of *CMAS* on Sintered 3YSZ Pellets

A THESIS SUBMITTED IN PARTIAL FULFILLMENT
OF THE REQUIREMENT FOR THE DEGREE OF

Bachelor of Technology
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Under the guidance of
Prof. SUDIP DASGUPTA

Submitted By

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CERTIFICATE

This is to certify that the project entitled "**Synthesis of 3 Mol% Yittria Stabilized Zirconia (3YSZ) and Study on Corrosion Behavior of *CMAS* on sintered 3YSZ Pellets**" submitted by **SAKET JAISWAL** is a genuine work performed by him under my guidance required for the **Bachelor of Technology** degree in **Ceramic Engineering** at **National Institute of Technology, Rourkela**.

To the best of my knowledge, this thesis is very authentic and none of its matter has been submitted anywhere else for the award of degree or diploma.

Sudip Dasgupta

Professor Dr. SUDIP DASGUPTA **Date:** 11/05/2015

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CONTENTS

ABSTRACT

The present work describes the corrosion behavior of CMAS (CaO-MgO-Al_2O_3-SiO_2 phase) on the Yttria-Stabilized Zirconia (YSZ) used for thermal barrier coating.

CMAS deposited on YSZ pellets and at high temperature it forms glassy phases and wets the surface of YSZ pellets and gets infiltrated into the surface. CMAS reacted with YSZ and form several compounds showing degradation of YSZ material meanwhile yttria gets dissolved in the CMAS solution and induced tetragonal to the monoclinic transformation which is associated with the volume expansion and hence causes cracks formation.

Our objective is to synthesize Yttria-Stabilized Zirconia(YSZ) by using 3mol%Y_2O_3 by chemical precipitation method, preparation of CMAS solution and study the corrosion and degradation behavior of YSZ pellets on which CMAS was deposited.

In the first part of work stabilization of tetragonal zirconia phase at different sintering temperatures were studied and it revealed that totally tetragonal phase was retained up to 1300^0C. So we used 1300^0C sintered pellets for our experimental work because it contains a high amount of tetragonal phase as well as and it has desired amount of porosity essential to lower the thermal conductivity of coating material.

In the result section, XRD of CMAS deposited YSZ pellets and the FE-SEM of reaction interface between YSZ and CMAS region were studied and it shows the degradation of YSZ material in the presence of CMAS.

List of figures and tables

CHAPTER 1

GENERAL INTRODUCTION

1.1 Introduction to Zirconia

Zirconia is the most important structural ceramic and refractory material with a wide range of application areas. There are three polymorphic forms of zirconia [1][2]:

- Monoclinic phase ($<1170^0$C) is the room temperature stable form
- Tetragonal phase ($1170 - 2370^0$C)
- Cubic phase($>2370^0$C)

For major application areas, we need to stabilize high-temperature forms (t-ZrO_2 and c-ZrO_2) at room temperature. For this variety of stabilizing agents used such as Yttria, Magnesia, Ceria and Calcium Oxide.

1.2 Properties of Zirconia

By stabilizing high-temperature form at room temperature, zirconia has some unique properties such as high ionic conductivity, fracture toughness, strength, high thermal expansion and low thermal conductivity. Thus, these properties make it suitable for thermal barrier coating application which is the main concern of this present work.

1.3 Major research on Zirconia

Garvie [10] propose the critical size of the crystallite for tetragonal to monoclinic transformation He proposed a relation:

$$(G_t - G_m) + S_t \gamma_t \leq S_m \gamma_m$$

Where

G = molar free energy

S = surface area of the single crystal particle.

It was observed that for stabilizing t- phase, the particle size must be $\leq$ 30 nm. For cubic to tetragonal phase transformation, the critical crystallite size is about 2 nm. [11]

1.4 Degradation of YSZ Coating

When YSZ coating were exposed to the high-temperature combustion environment it degraded due to phase transformation from t-ZrO_2 to m-ZrO_2. Also, another reason which affects the coating is foreign air particles calcium-magnesium-alumina-silicate (CMAS) get deposited on it. These deposit form glassy phase at high temperature which wets the YSZ coated material and due to its porous structure it get infiltrated into the surface. During cooling it gives residual compressive stress while heating it expands and gives tensile stress. Due to repeated cooling and heating the stress causes crack formation and hence cause failure of the coating material.

1.5 Outline of the Present Report

A brief introduction of the topic has been presented in this chapter. In the next chapter, literature has been presented along with the objective and motivation of our work. Chapter 3 describes experimental work regarding our project in details. Chapter 4 discussed the results and seeks to provide the explanation to the results. In the final chapter, conclusions of the work are summarized.

CHAPTER 2

LITERATURE REVIEW

2.1 Stabilization of Zirconia

As we know the high temp form of zirconia are tetra and cubic. When zirconia is cooled from high temperature there is a martensitic transformation from t-ZrO_2 to m-ZrO_2 which is associated with 3-4% volume expansion hence lead to failure of zirconia [3]. Therefore, the use of zirconia is limited. To increase its application area many works have been done to retain its high temp at room temperature.

For which various stabilizing agents are used such as Y_2O_3, CaO, MgO, and Ceria [4].

There are three types of zirconia stabilization

a) Fully stabilized zirconia (FSZ): it contain total cubic zirconia phase. The amount of Y_2O_3 needed for this should not less than 8 mol%.
b) Partially stabilized zirconia PSZ): it may contain (cubic+ tetragonal) or (cubic+ monoclinic) or (cubic+ mono +tetra) phase simultaneously.
c) Tetragonal zirconia polycrystalline (TZP): it contains totally tetragonal phase.

In the present work we used 3mol% Y_2O_3 as stabilizing agent to get tetragonal zirconia polycrystalline (3Y-TZP).

2.2 Zirconia as thermal barrier coating

Thermal barrier coating (TBC) is used to provide insulation to the hot section components of gas turbine engines, turbine blades of aircraft engines diesel engines and power generation systems [5-7]. It protects metallic components from high-temperature environment [8].

Properties for a material to be used as thermal barrier coatings are:

- Low thermal conductivity
- High thermal expansion coefficient
- Thermal stability
- High refractoriness

In respect to these properties, yttria-stabilized tetragonal zirconia is used for thermal barrier coating application.

2.3 Thermal barrier coating (TBCs)

A Thermal Barrier Coating system comprises of following sections:

- Ceramic topcoat for thermal insulation,
- A thermally grown oxide(TGO) scale mainly Al_2O_3,
- A metallic bond coat which provides corrosion and, oxidation resistance and
- For load bearing, a *super alloy* substrate is used

TBCs are exposed to the combustion environment combined with air- ingested foreign particles. These particles get deposited on the hot TBC surfaces as molten CaO-MgO-Al_2O_3-SiO_2 (CMAS) and infiltrate into the porous TBCs surface of the blades. While cooling, these deposits form glassy phase and cause the thermal expansion mismatch between CMAS and the coated material, thereby leading to the TBCs degradation. In recent years, this kind of failure mode of TBCs has attracted a lot of attention. Various studies have done on the high-temperature corrosion of TBCs by CMAS attack [9-14].

CMAS (CaO-MgO-Al_2O_3-SiO_2 phase): it is the acronym of CaO, MgO, Al_2O_3 and SiO_2 [15-18].Its melting point is around 1250 C. CMAS composition consists of (in mol %)

35 CaO, 10 MgO, 7 Al_2O_3 and 48 SiO_2

2.4 Objective of the work

The present work seeks to deal with

a) Synthesis of yttria stabilized zirconia using ammonium hydroxide as a precipitating reagent.
b) Sintering of 3YSZ Pellets at different temp and study the phase transformation.
c) Preparation of CMAS and study the corrosion behavior of it on 3YSZ pellets.at high temperature.

There is degradation in coating due to the tetragonal to monoclinic transformation at high temperature and also due to the environmental CMAS deposition. As the unavailability of equipment, we can't provide a whole TBC system. So we did experiments only on coating ceramic material in the form of very thin pellets and study the microstructure change and reactions between YSZ and CMAS.

CHAPTER 3

EXPERIMENTAL WORK

3.1 Synthesis of Yttria stabilized zirconia (YSZ)

Yttria as stabilizing agent used to retain the high-temperature form of zirconia at room temperature. 3 mol% Y_2O_3 is used in this synthesis process.

Chemicals used are:

- Zirconium oxy- chloride octahydrate $ZrOCl_2.8H_2O$
- Yttrium oxide Y_2O_3
- Ammonium hydroxide NH_4OH
- HCl and ethanol

NH_4OH is used as a precipitating agent. First Y_2O_3 is dissolved in conc. HCl solution along with an addition of ethanol to increase the yttria solubility. The above solution was kept over-night on a magnetic stirrer so that a clear solution will form i.e., yttrium chloride.

$$Y_2O_3 + 6HCl \rightarrow 2YCl_3 + 3H_2O$$

Then this clear solution was poured into pre- prepared $ZrOCl_2.8H_2O$ solution. Both of these solutions were mixed properly on the magnetic stirrer.

Now the precipitating agent NH_4OH were added drop wise to above mixed solution. Then after some time as the concentration of ammonium hydroxide increased, precipitate formation occurred. We added ammonium hydroxide till pH ~ 9 around so that all $ZrOCl_2.8H_2O$ changes to $Zr(OH)_4$.

This precipitate was washed several times by centrifugation so that impurities such as chloride and ammonia were removed totally. And we got a precipitate of $Zr(OH)_4$ only which was collected in a petri dish and kept for drying for one day at a temperature of 50^0C around.

The dried material where milled into small size particles and then it was calcined at 600^0C for 4 hours to get zirconia. Then XRD of the powder zirconia were done to identify the phase formation which is discussed in next chapter.

For our experimental work, we need ZrO_2 pellet that's why pellets were formed by pressing and a small amount of binder (PVC) was used.

The thickness of the pellet was kept very small as possible as so that it will reflect the thermal barrier coating as then we can study the CMAS behavior on this pellets.

Apparent porosity and bulk density of the pellets were tested to determine the porous nature of the YSZ pellets.

3.2 CMAS Preparation

Chemicals used:

$Ca(NO_3)_2$, $Mg(NO_3)_2$, $Al(NO_3)_3$, SiO_2

Composition of CMAS (in mol %): 35 CaO, 10 MgO, 7 Al_2O_3 and 48 SiO_2

Half mole CMAS solution was prepared by dissolving above chemicals in the water and stirred form some time. Then this solution was poured over sintered pellets of YSZ drop wise and simultaneously we were drying it so that a thick layer of CMAS could be obtained. Then the pallets were fired at 1300^0 C for 6 hrs for four times.

CHAPTER 4

CHARACTERIZATION

4.1 X-Ray Diffraction

Phases of synthesized 3YSZ powder at different sintering temperatures, and CMAS deposited and corroded YSZ pellet sample were evaluated using XRD (Philips, Hollnad) with Cu-Kα (λ=1.54 Å) at a scanning rate of 0.05 and scanning range of 20^{o}-80^{o}.

4.2 Apparent Porosity and Bulk density Measurement

Apparent porosity and bulk density of sintered 3YSZ pellets were measured. The pellets were soaked in boiled water for 45 minutes. And the AP and BD were calculated by following formulas.

Apparent Porosity (AP) = (W-D)/ (W-S) * 100

Bulk density (BD) = D/ (W-S) *100

Where

W = Soaked weight

D = Dry weight

S = Suspended weight

4.3 Field Emission Scanning Electron Microscope (FE-SEM)

Microstructure of the sintered pellets of 3YSZ and CMAS deposited corroded 3YSZ pellet were observed using FE-SEM (NOVA, FEI) at 10kV.

CHAPTER 5

RESULT AND DISCUSSION

5.1 XRD of YSZ powder sample

XRD analysis of powder sample at different sintering temperature (600, 1300 and 1500^0C) has been done to identify the phases present in the YSZ powder sample.

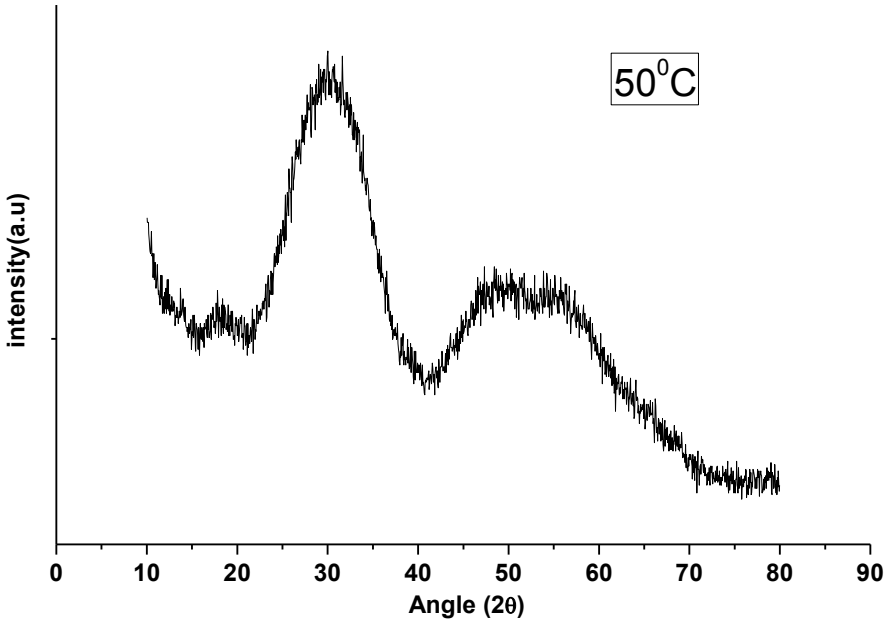


Fig 1 -: XRD of dried 3YSZ powder at 50^0C.

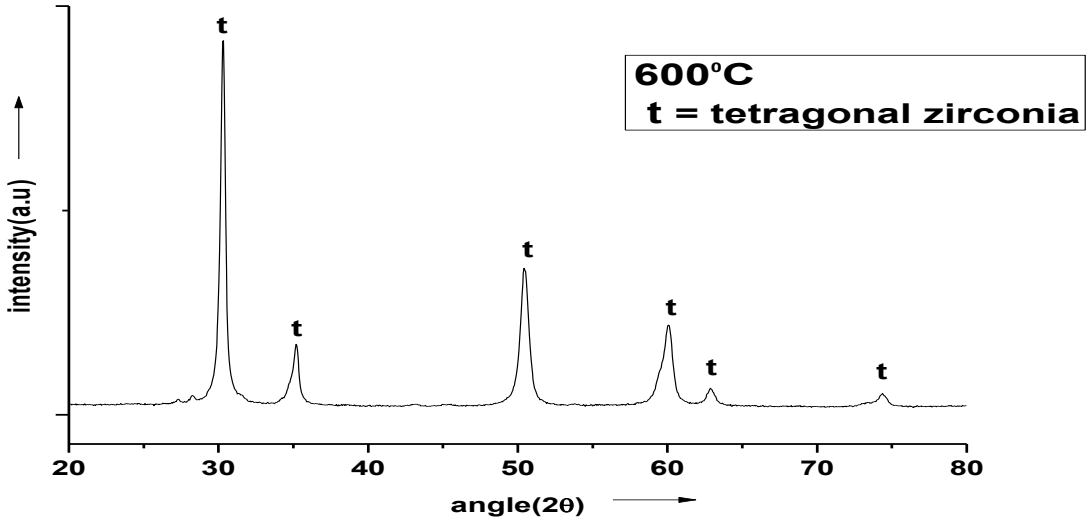


Fig 2 -: XRD of calcined 3YSZ powder at 600^0C.

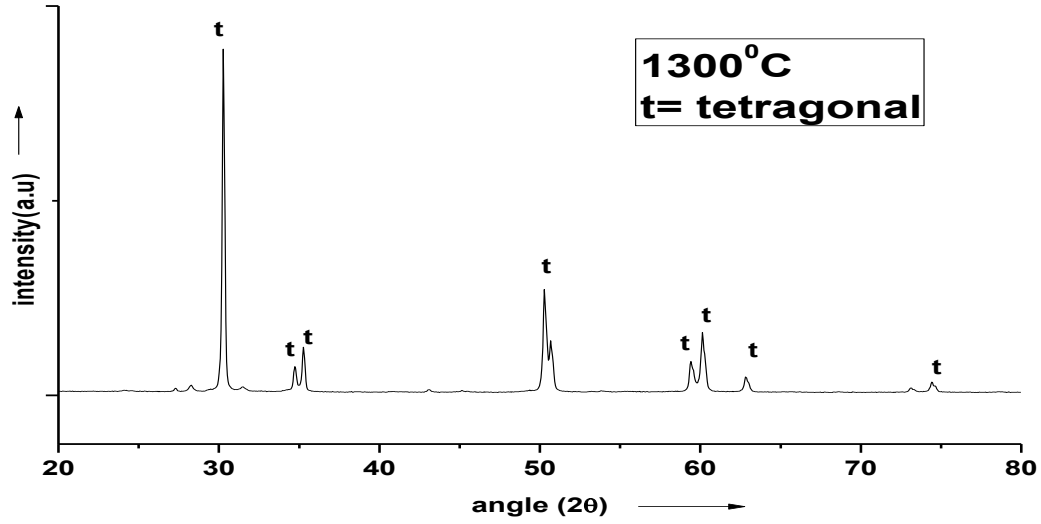


Fig 3 -: XRD of sintered 3YSZ powder at 1300^0C.

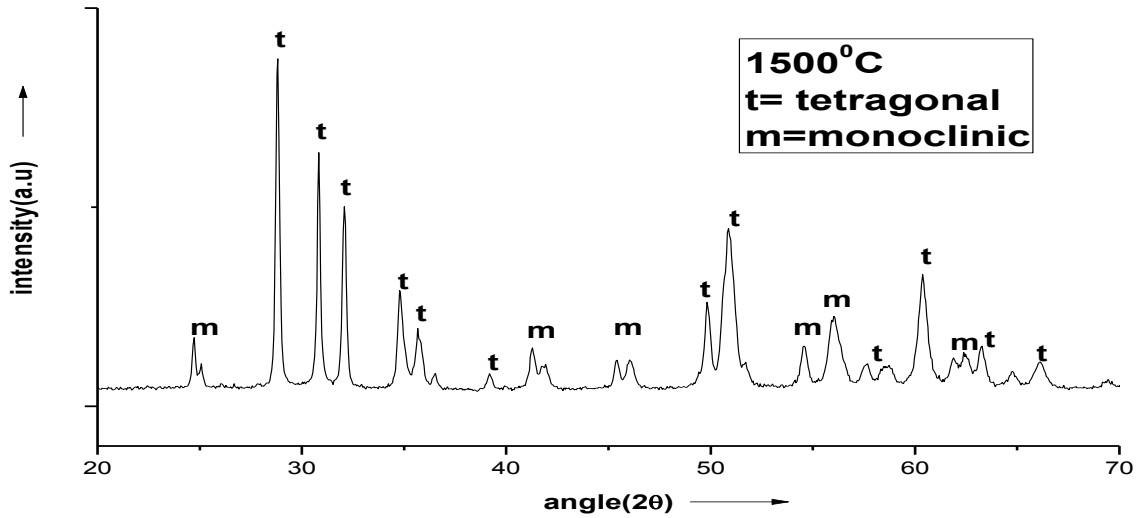


Fig 4 -: XRD of sintered 3YSZ powder at 1500^0C.

It was observed that the dried sample at 50^0C shows amorphous nature due to the presence of hydrous zirconia. On heat treatment, it crystallizes into tetragonal ZrO_2 as shown in XRD of powder calcined at 600^0C. On sintering at 1300^0C it retains tetragonal phase but there is some amount of negligible amount of monoclinic phase present in it. If sintering temperature increases to 1500^0C, some phase transformation occurs due to the slow diffusion of yttria into zirconia.

Our desired phase is tetragonal so a 1300^0C sintered YSZ is used for experimental work.

5.2 APPARENT POROSITY AND BULK DENSITY MEASURMENT

This is done to measure the density of the YSZ pellets and its porosity so that CMAS can infiltrate into the surface and react with YSZ. As we need the porous nature of coating material so that its thermal conductivity get decreased and better for thermal insulation.

Sintered pellets at 1300^0C	Apparent Porosity (%)	Bulk Density(g/cc)	Bulk Density (%)
1	23.65	4.429	72.72
2	21.81	4.459	73.21
3	17.70	4.469	73.38

Table 1 : AP and BD values for YSZ pellets sintered at 1300^0C.

5.3 XRD of CMAS deposited 3YSZ pellets

Intensity vs 2Ɵ plot (fig 5) has been drawn from XRD result of CMAS deposited YSZ pellet fired several times at 1300^0C for 6 hrs.

As we seen in fig 5 some monoclinic phase induced this is due the fact that on high temp. , Y_2O_3 get dissolve in CMAS and facilitate the transformation.

It is observed that CMAS reacted with zirconia and formed some compounds like zirconium silicon, zirconium magnesium oxide, calcium zirconium oxide and aluminium zirconium respectively. This shows that YSZ pellet top surface get corroded, hence degradation of YSZ observed.

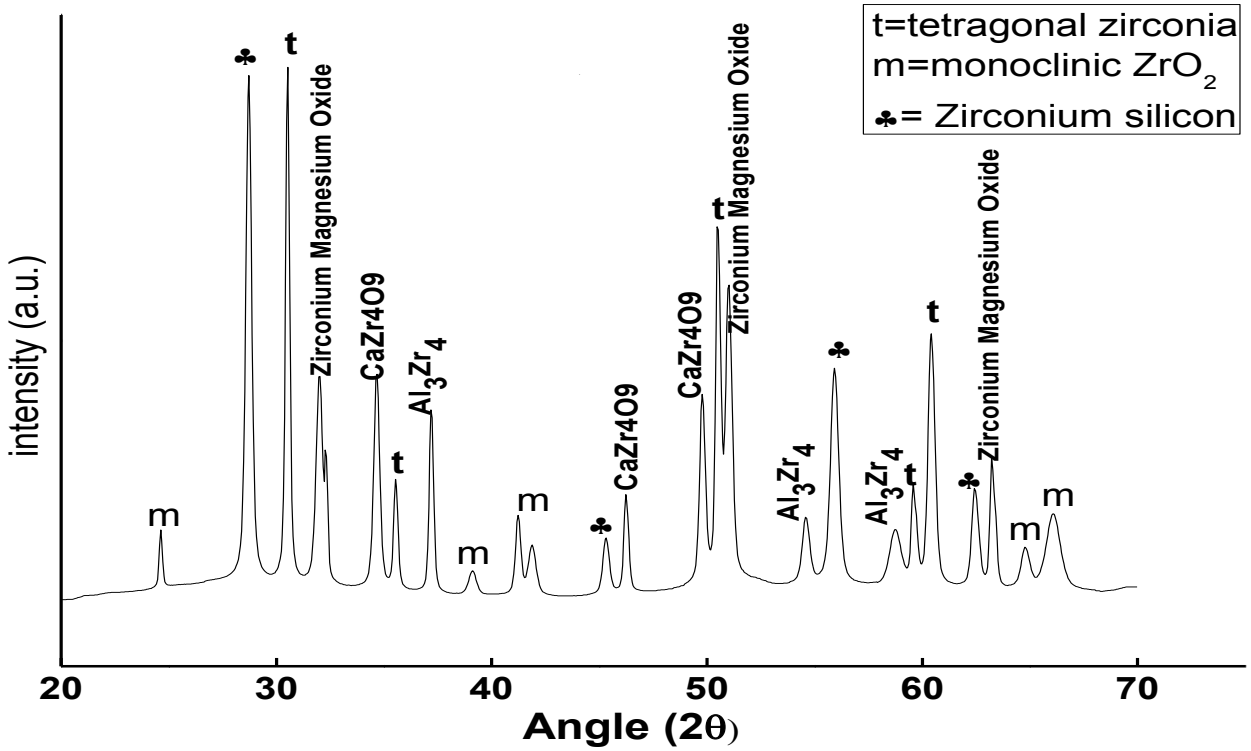
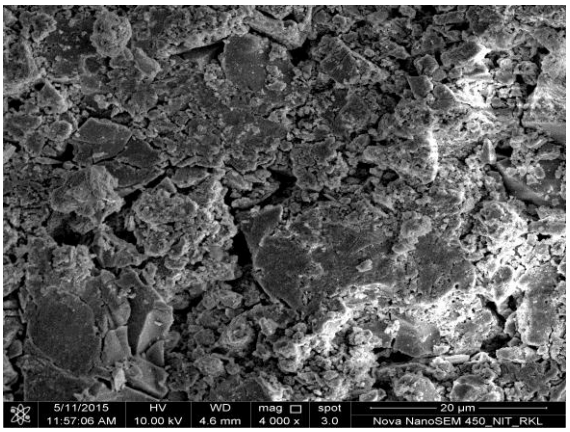


Fig 5: XRD of YSZ to determine different phases formed due to the reaction between YSZ and CMAS

5.4 Field Emission Scanning Electron Microscope (FE-SEM)

In fig 6(b) we can see that unreacted grains of t- zirconia that was densified because of subsequent heating at 1300°C as a result density of the tetragonal zirconia matrix was increased due to which elasticity and thermal conductivity of zirconia matrix was enhanced which results in higher heat flux and enhanced corrosion at high temperature.



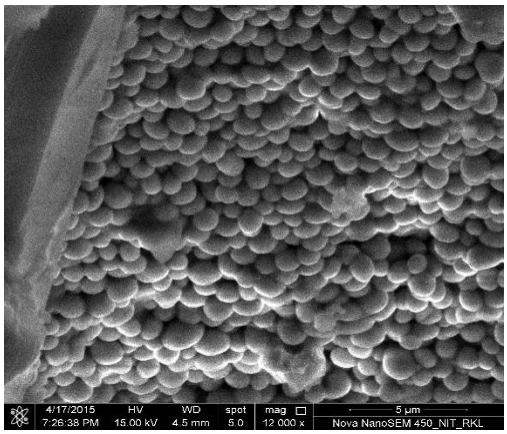
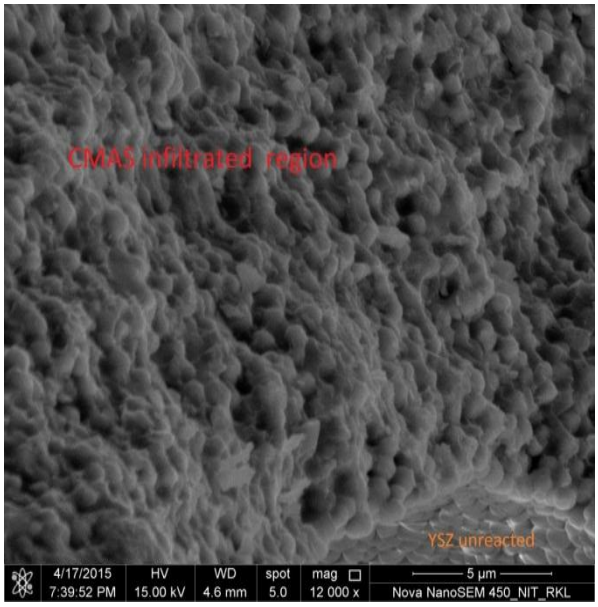
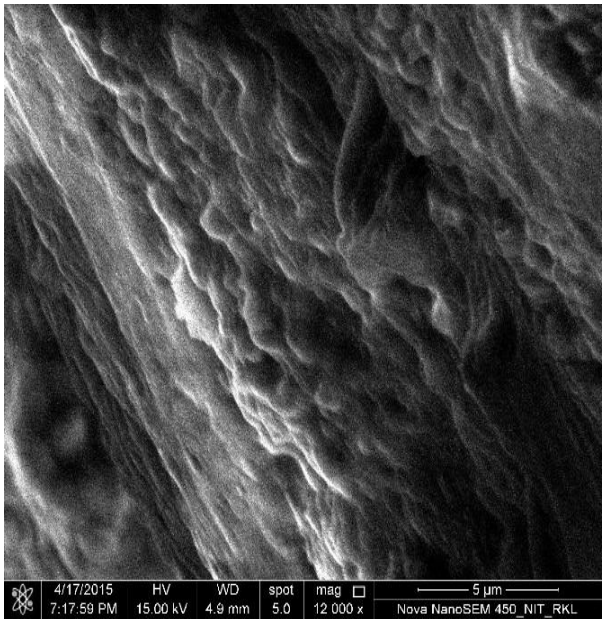


Fig 6 a) YSZ grains before CMAS deposition b) Unreacted densified YSZ grains





7(a) 7(b)

Fig 7 a) SEM image of infiltrated region at the interface of CMAS and YSZ pellet b) Glassy phase formation due to the reaction between CMAS and YSZ

In fig 7(a) we can see that infiltration of CMAS into the YSZ material where it reacted with YSZ to form glassy phases (fig 7-b).

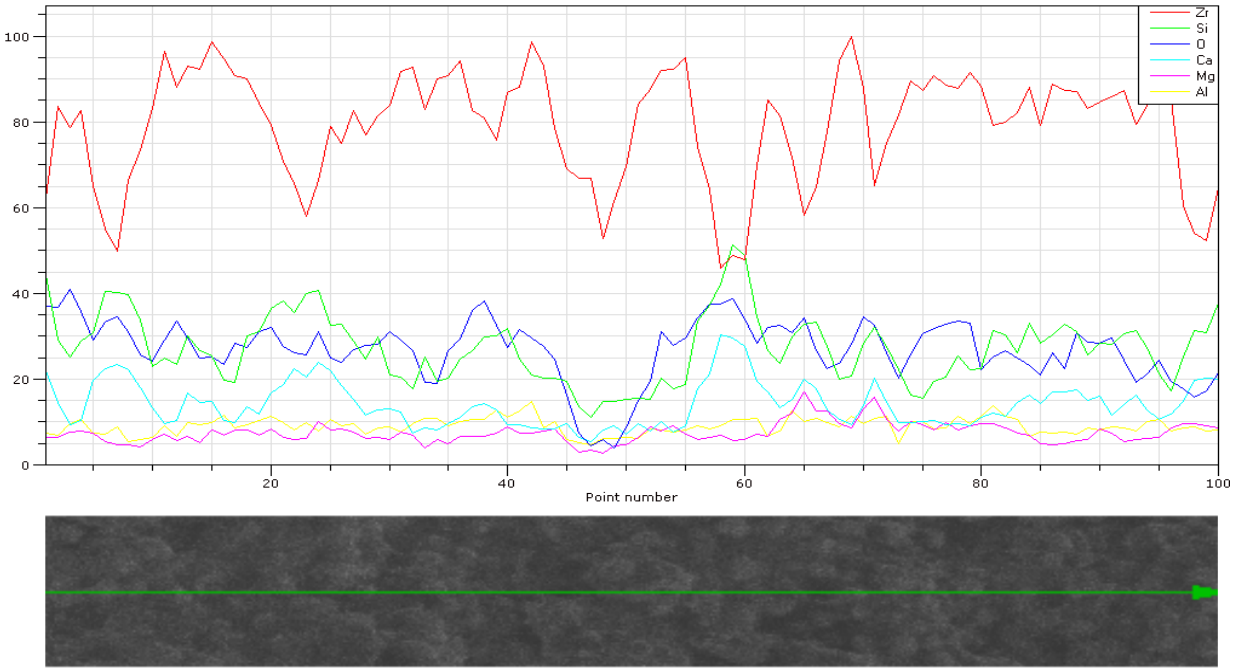


Fig 8(a) Elemental concentration at the depth of 10µm from the YSZ surface

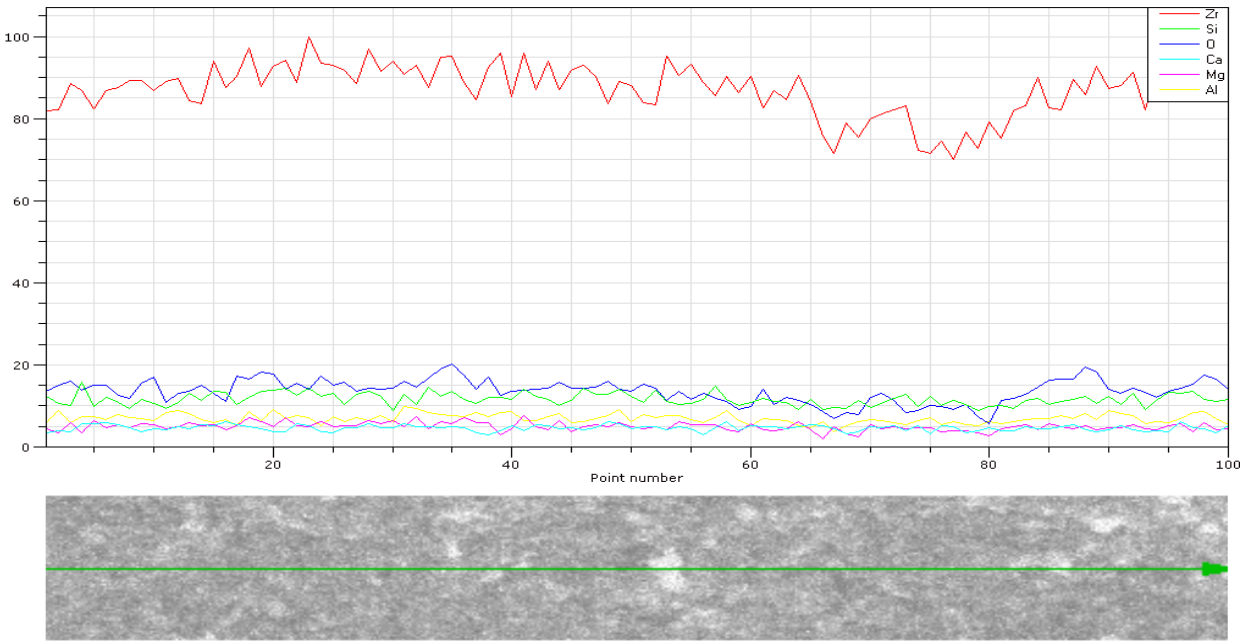


Fig 8(b) Elemental concentration at the depth of 500µm from the YSZ surface

As infiltration of CMAS occurs through the surface of YSZ by diffusion at high temperature, the amount of CMAS concentration will depend on penetration depth. As evident from the fig 8(a) and 8 (b) we can say that the concentrations of Si and Ca are much higher than Al and Mg which shows that the rapid penetration of Si and Ca at 1300^0C. [10]

From the table 2(a) and 2(b) we can say that the amount of CMAS present in tetragonal zirconia matrix is decreased as we go deeper into the surface.

Elemental distribution of CMAS in zirconia matrix at infiltrated region is shown in fig 9 suggest that Zr atoms are being surrounded by CMAS atoms such as Ca, Si, Al and Mg respectively. Corrosion results in thermal expansion mismatch between YSZ and CMAS glassy phase results in crack propagation during subsequent heating and cooling cycle and hence failure of the top coat YSZ observed.

In fig 10 shows that the cracks were formed beneath the surface of YSZ where CMAS deposited. At high temperature, this CMAS form glassy melt which get infiltrated into the surface of the YSZ pellet. During cooling it gives compressive stress while on heating it gives tensile stress to the matrix. Therefore by repeated compressive and tensile stresses, the crack propagates and cause failure of YSZ coating onto turbine blades.

Table 2(a): Elemental concentration at the depth of 10μm from the YSZ surface

Element	Atomic number	series	Net unn.[wt %]	Normal conc.[wt%]	Atom Conc.[at.%]
Zr	40	L-series	41.08	52.47	16.61
O	8	K-series	21.27	27.17	49.02
C	6	K-series	8.35	10.67	25.64
Ca	20	K-series	3.58	4.57	3.29
Si	14	K-series	2.62	3.34	3.44
Mg	12	K-series	0.74	0.94	1.01
Al	13	K-series	0.65	0.84	0.99
		total	78.29	100.00	100.00

Table 2(b) Elemental concentration at the depth of 500 μm from the YSZ surface

Element	Atomic number	Series	Net unn.[wt %]	Normal conc.[wt%]	Atom Conc.[at.%]
Zr	40	L-series	40.29	59.52	19.63
O	8	K-series	20.35	30.06	56.53
C	6	K-series	6.10	9.00	22.55
Ca	20	K-series	0.51	0.76	0.57
Si	14	K-series	0.36	0.53	0.56
Mg	12	K-series	0.09	0.13	0.16
Al	13	K-series	0.00	0.00	0.00
		total	67.69	100.00	100.00

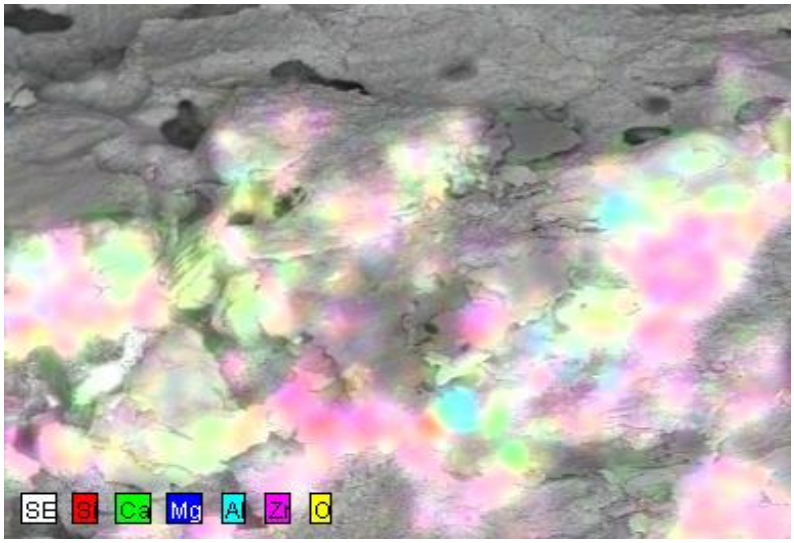


Fig 9 distribution of elements at CMAS infiltrated region.

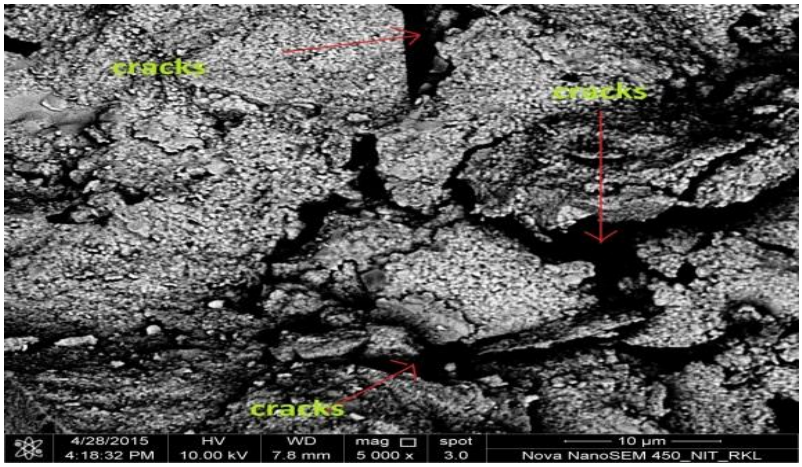


Fig 10 showing YSZ TBC degradation i.e., cracks formations

CHAPTER 6

CONCLUSIONS

i) For TBC application, desired phase of zirconia is tetragonal which is achieved up to the sintering temp of 1300^0C. Above this temperature if sintering is done there will be some phase transformation.

ii) CMAS reacted with YSZ to form some oxides such as Zirconium Magnesium Oxide, Calcium Yttrium Oxide, and some glassy phases which shows corrosion nature of CMAS.

iii) Yttria in YSZ layer as a stabilizer was dissolved in CMAS glass and caused accelerated monoclinic phase transformation which is associated with volume expansion results in cracks generation.

IV) CMAS forms glassy phase (melt) at high temp which wets the YSZ surface and infiltrated into it. During cooling, it gives residual compressive stress while on heating it expands and gives tensile stress to the structure. Due to the repeated compressive and tensile stresses, cracks propagate and cause failure of the YSZ pellets.

Therefore, CMAS deposition is very detrimental for YSZ thermal barrier coating applied at the surfaces of the hot section components in gas turbine engines and turbine blades of aircraft.

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